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Oxidation behavior at moderate temperature under dry and wet air of phenolic resin-derived carbon

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Abstract:

The oxidation behavior of carbon materials has been investigated at temperatures less than 773 K using isothermal thermogravimetric analyses under dry and wet air. Bulk samples obtained by the pyrolysis of phenolic resin have been characterized using X-ray diffraction and elementary analysis. X-ray photoelectron spectroscopy and Raman spectroscopy have been performed to analyze the surface and subsurface. The carbon structure has a poor organization state and a gradient in the oxygen concentration and structure between the surface and the bulk is revealed. The material is more reactive under wet air than dry air in terms of oxidation rates as determined between 623 and 773 K. The apparent activation energies are respectively 122 ± 6 kJ/mol in dry air and 102 ± 6 kJ/mol in wet air.

Key words: Phenolic Resin; Carbon materials; Thermogravimetric Analyses; Oxidation behavior; Reaction Kinetics; Structure

Introduction

The general oxidation mechanism of carbon materials in air has been investigated for many years. Characteristics of carbon such as surface chemistry, microstructure, crystallinity, surface morphology and the presence of impurities play a key role on the reaction kinetics [1-5]. Today, it is well established that the reactivity of carbon may be discussed in relation with surface properties and carbon structure [1-7]. Environmental oxidizing conditions containing moisture can influence the oxidation rate of carbon. The reaction between pure water vapor and carbon at temperatures below 773 K is considered as negligible. In the presence of oxygen, some discrepancies in published results can be noticed such as the decrease or increase of reactivity, depending on the nature of carbon samples [8-11].

Within the framework of the French project COMPTINN (“COMPosites Tièdes et INNovants”), low cost 2D carbon/carbon (C/C) composites have been considered for some structural parts of civil aircraft engines operating between 423 and 673 K. The durability of C/C composites in this temperature range remains unknown since they have never been developed for this particular application. One of the objectives of the COMPTINN project

was to correlate the chemical reactivity of the constituents of the selected C/C composite (fibers, matrix) with their structural organization. One of the low-cost processes considered for the carbon matrix is the impregnation and pyrolysis of a phenolic resin. The oxidation behavior of non-graphitizable carbon such as phenolic resin-based coke, has been the subject of investigations in dry air [6, 12, 13]. Most studies were related to the elaboration of electrodes and focused on the activation process that is the development of porosity more than on kinetic analysis. Chang and Rhee have studied phenolic resin-based carbon, heat treated at temperatures ranging from 1273 to 2673K. The results indicated that oxidation rate decreases with increasing heat treatment temperature [6]. The authors showed that the surface area and the amount of impurities were both reduced after heat treatment and they suggested that both of these factors influence the oxidation rate. The weight losses due to oxidation were recorded using thermogravimetric analysis at temperatures between 697 and 965 K and an average value of the activation energy of 175 kJ/mol were determined. The oxidation mechanism of phenolic resin-based carbon in wet air at temperatures below 773 K has not yet been investigated. Several studies performed between 573 and 773 K were related to soot oxidation [14, 15]. The values of activation energy for carbon-oxygen reaction range between 130 and 170 kJ/mol. As it was said above, it has been shown for a long time that carbon – water reaction is negligible below 773K [8], but some studies on C-O₂-H₂O system have shown a significant influence of water vapor on carbon oxidation [14, 15]. Despite its importance for application of C/C composites, published data on oxidation of phenolic resin based carbon in wet conditions are scarce.

This work establishes and compares the oxidation kinetic laws of phenolic resin-based carbon under dry and wet air. The independent control of the oxidizing species partial pressures, O₂ and H₂O in the ageing gaseous environment, allows determining the partial reaction order related to oxygen and water in the kinetic law. Physico-chemical and microstructural characterizations of carbon samples have been performed using some classical methods such as elemental analysis, X-ray photoelectron spectroscopy (XPS), X-ray diffraction and Raman spectroscopy. Active site area measurements are used to examine the variation of carbon samples reactive surfaces before and after oxidation in dry and wet air. The influence of moisture on the oxidation behavior is then discussed in relation to the adsorption processes (surface composition) and the carbon structural organization.

1. Experimental

1.1 Materials

Bulk specimens of carbon were prepared by curing and pyrolyzing a resol-type phenolic resin. Thin plates of cured resin were slowly pyrolyzed in flowing nitrogen in a tubular furnace with a heating rate of 2 K/min, up to 1273K. Some samples labeled C₋₁₈₇₃ were heat treated up to 1873K in tubular furnace under vacuum. The size of the resulting carbon pieces, referred to as C_{-carbonized} in the following, is typically 8.5mm x 2.5 mm x 5mm.

1.2 Physico-chemical and structural characterizations

The carbon, hydrogen, oxygen, sulphur, nitrogen and metal impurities concentrations of the specimens were quantified by elemental analysis (ISA-CNRS, Villeurbanne, France).

The true densities of samples were measured by helium pycnometry, using an AccuPyc 1340 pycnometer (Micromeritics, France).

The surface functional groups are a key point to understand low temperature carbon reactivity. The samples surface properties were investigated using X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption with quantitative mass spectrometry analysis (TPD-MS). XPS experiments were carried out with a XPS VG ESCALAB 220i-XL system (PLACAMAT-CNRS, Pessac, France). The O/C atomic ratios were computed from survey spectra obtained at constant pass energy of 150 eV with a monochromatic AlK α radiation (1486.6 eV). The analyzed depth was close to 5 nm. In order to study the concentration gradient in the bulk material, ionic ablation was used to remove a carbon layer with a depth up to 14nm.

In addition to XPS, TPD-MS is a powerful method to study carbon surface chemistry [16, 17]. Experiments were done with a custom-made experimental setup under vacuum (maximum pressure of 10⁻² Pa). The carbon sample was deposited in a fused silica tube and heated up to 1223 K with a heating rate of 5 K/min. On-line quantitative analysis of CO, CO₂, H₂, H₂O, N₂ and O₂ was done and the desorption rates and temperatures could be related to the surface functional groups [16].

X-ray diffraction (XRD) analysis was performed on thin sections cut in the carbon blocks using a Bruker D8 advance diffractometer equipped with a Cu-K α_1 X-ray source. A conventional approach was used to obtain the crystallographic parameters [18]. The interreticular distance corresponding to the (002) reflection was determined from the angular position (θ_{002}) of the maximum intensity of the (002) peak. The average length of the crystallites along the c-axis L_c and the layers lateral extent L_a, were determined respectively from the full width at half maximum of the (002) peak, using the Scherrer formula (with K=0.9) and from the full width at half maximum of the (10) peak, using the Warren formula (K=1.84) [19].

The Raman spectra ($\lambda = 632.8$ nm) were recorded with a Labram HR microspectrometer (from Horiba Jobin Yvon), on polished cross-sections of the specimens. The full width at half maximum of the D band (FWHM_D) around 1350 cm⁻¹ in a useful assessment of the amount of in-plane structural disorder in the carbon layers [20]. Point measurements were recorded from across sections of C_{-carbonized} blocks, with a lateral resolution of about 1 μ m. The FWHM_D value was deduced after a base-line correction and a curve-fit of the spectra (with a Lorentzian function for the D band).

The surface morphology of the samples was observed by scanning electron microscopy (SEM, Hitachi-S4500). Thin slices of C_{-carbonized} were prepared using a JEOL argon ion slicer (EM-09100IS) device [21]. Structural characterizations of the resulting thin specimens were performed with a Philips CM30ST transmission electron microscope (TEM) (LaB6-300 kV).

Active surface area (ASA) measurements of the samples were performed using a furnace coupled with a mass spectrometer, according to a method described elsewhere [9]. A first

overall desorption of sample surfaces was carried out through a degassing step at 1073 K under vacuum for 15 min. The samples were then subjected to a controlled sorption step, without any carbon gasification, at 573 K under a low oxygen pressure (66 Pa) during 5h. The carbon samples were then outgassed to remove physisorbed species, and a thermally-activated desorption was performed by heating the specimens up to 1073 K at a heating rate of 10 K/min. The ASA measurement was determined from the amounts of CO and CO₂ evolved and quantified by mass spectrometry analyses.

1.3 Oxidation experiments

The oxidation tests were performed with a Setaram Setsys 1600 thermal gravimetric analysis (TGA) device equipped with a moisture control, as described previously [11]. The experiments were carried out in isothermal conditions at temperatures ranging from 623 to 773 K under a total pressure of 100 kPa, and with a constant gas flow of 2 normal L/h. The samples were first heated up to the working temperature under argon. The oxidizing gaseous environment was introduced only once the dwell temperature was reached.

The values of apparent activation energy were determined in dry and wet gas mixtures with respectively: (i) two oxygen contents, O₂/N₂ = 20/80 and 10/90, and (ii) three oxygen/moisture ratios, O₂/H₂O/N₂ = 20/05/75, 20/10/70 and 10/10/80. Partial reaction orders related to oxygen and water vapor were obtained at 673 K, with partial pressures of: (i) oxygen ranging from 5 to 100 kPa and (ii) water vapor from 5 to 20 kPa, while maintaining an oxygen partial pressure of 20 kPa. Under such conditions, the rate of oxidation is expected to be controlled by chemical reactions [22].

The determination of the apparent geometrical oxidation rate was based on the mass loss measurements related to the external surface area. Because the rate was determined at low burn-off level (between -0.5 and -2%) the change in surface could be neglected. The macroscopic kinetic laws of the carbon specimens were then established from the following Arrhenius equation (1).

$$k = k_0 \cdot \exp\left(\frac{-E_a}{RT}\right) \cdot \prod_i P_{ox_i}^{n_i} \quad (1)$$

Where k is the value of the apparent oxidation rate (in m/cm².s), k₀ the pre-exponential factor (in mg/cm².s.Pa^{∑_i n_i}), E_a the apparent activation energy (in J/mol), R the universal gas constant (8.314 J/mol.K), T the oxidation temperature (in K), P_{ox_i} the partial pressure of the oxidizing species i (in Pa) and n_i the partial reaction order related to the oxidizing species i.

2. Results

2.1 Physico-chemical properties

The true density of C_{-carbonized}, as determined using helium pycnometry, is 1.66 ± 0.02g/cm³. Such a low value is expected for non-graphitizable carbon heat treated up to 1273 K. More specifically, it is in agreement with the density obtained for phenolic resin-based carbon, as reported in reference [23] or [24].

The bulk and surface compositions of the carbon materials are respectively presented in tables 1 and 2. After pyrolysis, a small proportion of oxygen and hydrogen is detected. Metallic impurities are also present at very low concentration levels. The impurities, as Na and Ca, are known to modify the oxidation mechanisms [6]. This problematic will be later discussed in regard to the very low amounts of these impurities and to the morphology of the oxidized surfaces.

It is generally admitted that oxygenated chemical functions are naturally present at the surface of carbonaceous materials. XPS allows determining the nature of the atomic environments involved in these functions. Table 2 presents the O/C atomic ratios for the carbon samples measured directly from the free surface and after argon ion etching, 14 nm below the original surface.

Table 1: Elemental bulk analysis of the phenolic resin-based carbon samples

Samples	<i>Elemental composition</i>							
	<i>(weight %)</i>					<i>(ppm)</i>		
	C	H	O	N	S	Na	Ca	Zn
C-carbonized	98.1	0.3	1.0	0.3	<0.2	17	<20	<5

The O/C ratios are calculated from measurements of the surface areas of the C1s and O1s peaks on the XPS spectra. The analyses were performed after ion sputtering directly in the working chamber to properly describe the distribution of the oxygen atoms between the surface and the bulk. The carbon blocks exhibit an oxygen concentration gradient between the surface and the internal part of materials, with higher oxygen content close to the surface.

Table 2: Surface characterization of phenolic resin-based carbon materials by XPS spectroscopy

Samples	O/C close to the surface	O/C 14 nm below the surface
C-carbonized	0.14	0.03

TPD-MS spectrum of the carbonized sample exhibits a large peak of water between 423 and 773K (Figure1a). It should be mainly related to dehydration reactions between functional groups, which lead to anhydride and lactone formation. These last groups undergo further decomposition above 623 K to yield CO and CO₂. For temperatures above 973 K, the release of CO increases because of the decomposition of phenols and ether functions.

By comparison with XPS, TPD-MS analysis is a volumetric method. The amount of oxygen desorbed from C_{carbonized} sample was 560 μmol/g. Since the analysis was performed only up to 1073 K, the oxygen contained in the sample was not completely desorbed. Nevertheless, the amount measured corresponds to a very low value of the atomic ratio O/C, that is 0.007. This

low value confirms that the carbon material exhibits a strong oxygen concentration gradient between the surface and the sub-surface.

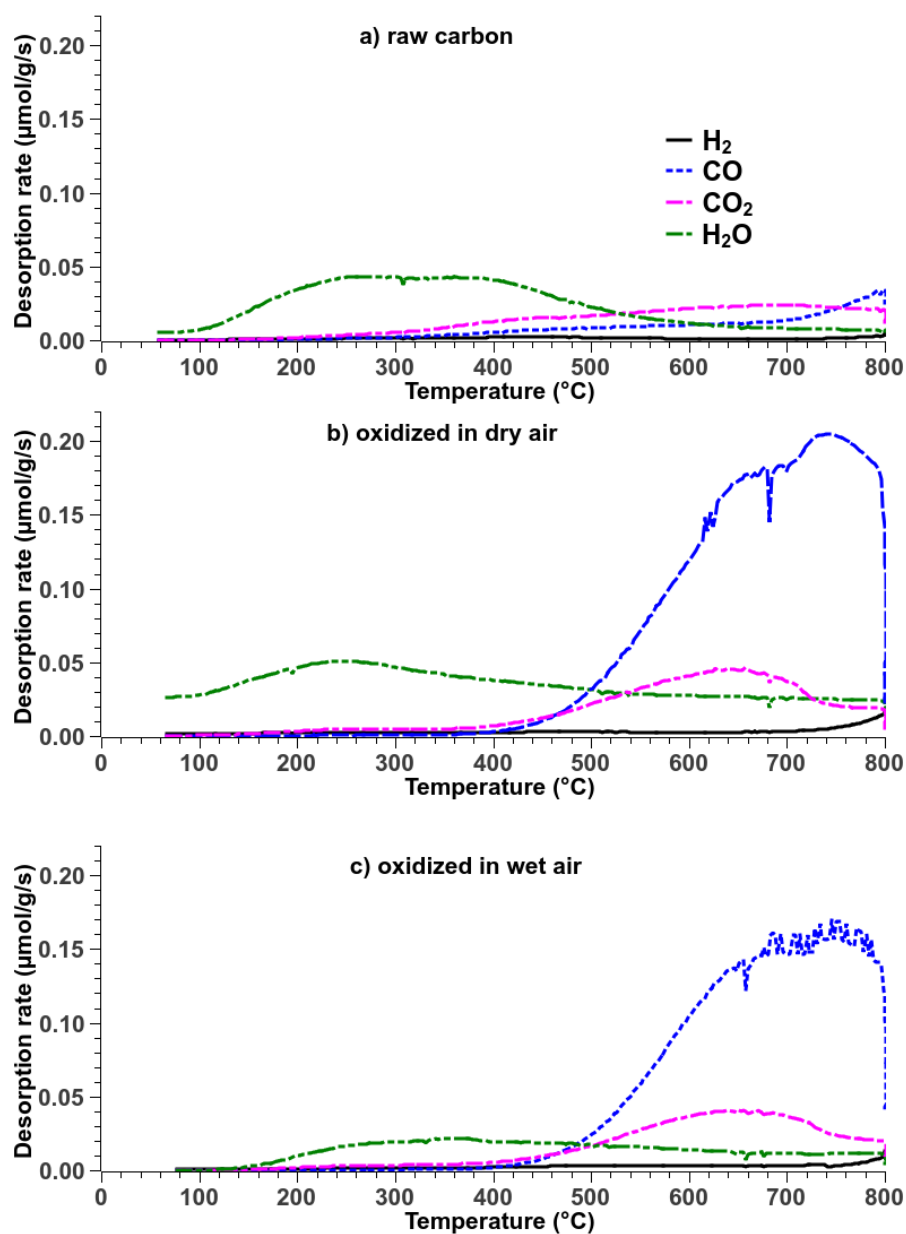


Figure 1 : TPD-MS analysis of $\text{C}_{\text{-carbonized}}$: a) raw, b) oxidized in dry air, c) oxidized in wet air

2-2 Structural properties

High resolution TEM

A HR-TEM analysis of the carbon material is presented in figure 2. The image is representative of a disordered structure with very short and distorted domains of only a few

layer stacks. Such a microtexture, associated to the low density, is typical of phenolic resin-based carbon heat treated at the same level of temperature [23].

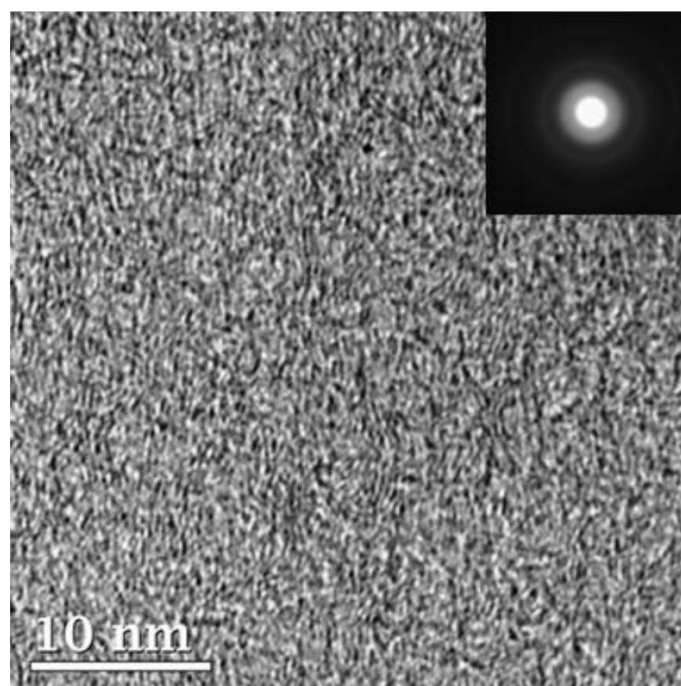


Figure 2 : HR-TEM characterization of phenolic resin-based carbon, *C-carbonized*

X ray diffraction

The XRD pattern of *C-carbonized* reported in figure 3 is characteristic of highly disordered turbostratic carbon, with broad (002) and (004) peaks and asymmetrical (10) and (11) peaks.

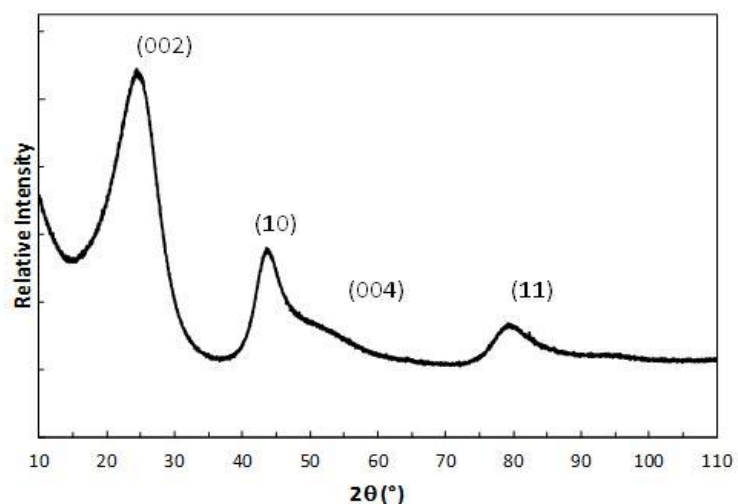


Figure 3 : X-Ray diffraction pattern of a phenolic resin-based carbon sample .

The following crystallographic parameters were derived from the XRD data : an interreticular distance $d_{002}=0.355(\pm 0.002)$ nm, an apparent crystallite size along the c-axis $L_c=1.2(\pm 0.1)$ nm and in lateral extension $L_{a10}=3.6 (\pm 0.3)$ nm. The value of the interreticular distance d_{002} is

slightly smaller than values reported elsewhere [6,23]. The L_c and La_{10} values are in the same order of magnitude as those generally obtained for phenolic resin-based carbon heat-treated at 1273 K.

Raman analysis

The Raman analyses were carried-out on polished cross-sections from regions close to the free surface to the core.

Two bands are observed in the spectra: the band assigned to disordered sp^2 carbon at 1325 cm^{-1} and the band typical for graphite (in-plane E_{2g} phonon) at 1580 cm^{-1} . Both bands are very broad and the D band is more intense than the G band, indicative of a particularly highly disordered structure. The spectrum is rather similar to the Raman spectra of phenolic resin-derived carbon obtained by Ko et al. [24]

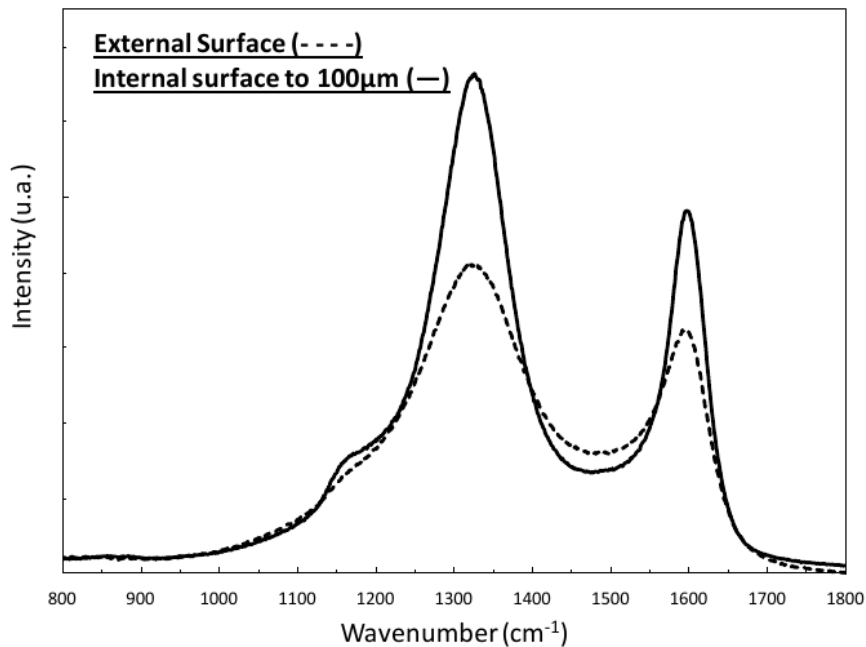


Figure 4 : Raman spectra of phenolic resin-based carbon after pyrolysis at 1273 K, from different localizations across the sample section.

The different spectra obtained near the surface and 100 μm deeper in the bulk of the same $C_{\text{carbonized}}$ block show that the sample microtexture is heterogeneous. The higher value of FWHM_D measured at the surface indeed reveal a structural state clearly poorer than that of the bulk (table 3). It should be mentioned that this phenomenon was observed repeatedly for different $C_{\text{carbonized}}$ block samples: Figure 3 and Table 3 are simply given as an illustration.

Table 3 : Variation of FWHM_D measured near the surface and in the bulk of a phenolic resin-based carbon block

Sample	$\text{FWHM}_D\text{ (cm}^{-1}\text{)}$	
	Surface	Middle
$C_{\text{carbonized}}$	165 ± 6	111 ± 1

2.3- Oxidation

Determination of the kinetic laws parameters

Figure 5 shows typical specific weight variations recorded in function of time during oxidation in dry air ($PO_2 = 20 \text{ kPa}$ and $PN_2 = 80 \text{ kPa}$), at temperatures ranging between 623 K to 773 K. Additional experiments were performed with different conditions of oxygen concentration in both dry and wet environments and in the same temperature range.

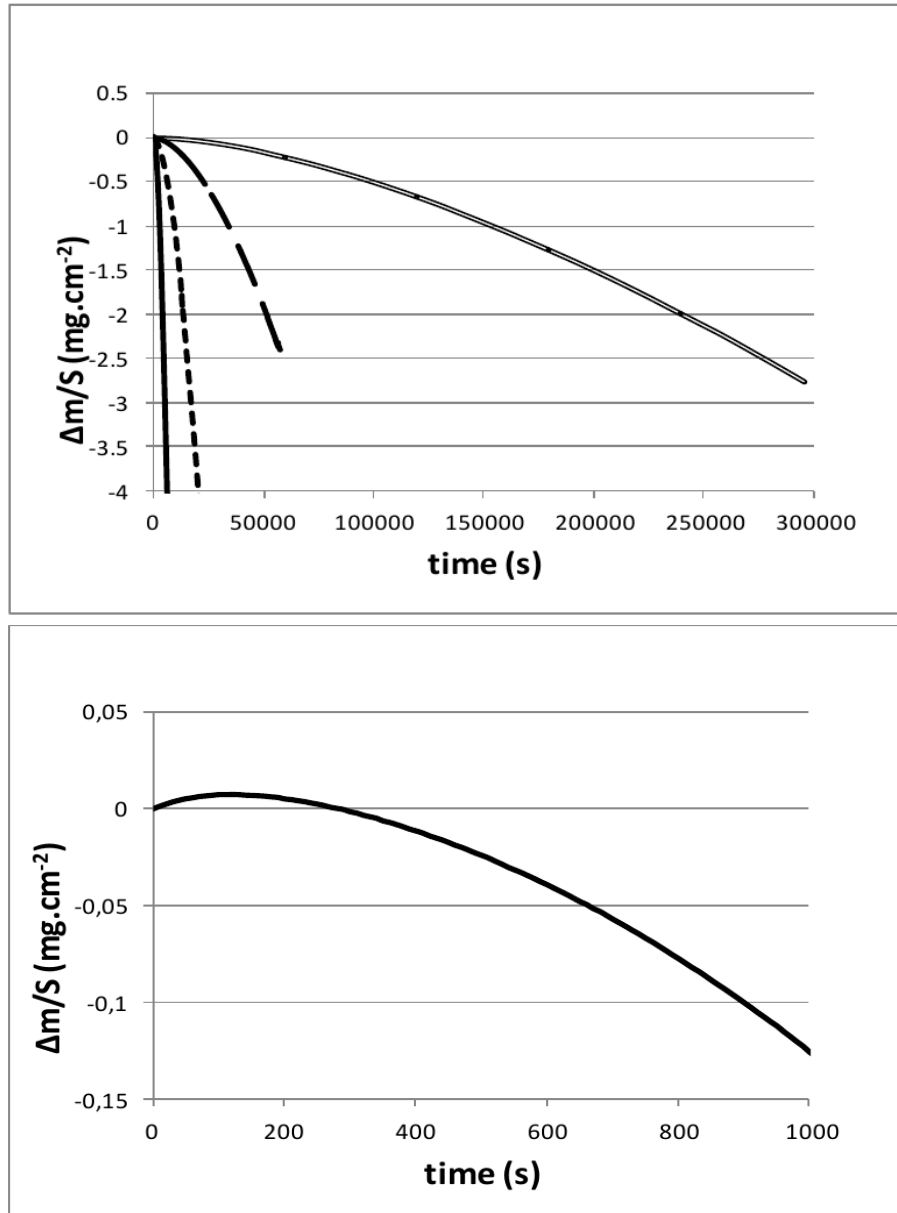


Figure 5: Specific weight loss of phenolic resin-based carbon recorded during oxidation in dry air ($PO_2 = 20 \text{ kPa}$ and $PN_2 = 80 \text{ kPa}$), at (—) 623 K; (— —) 673 K; (----) 723 K and (.....) 773 K.

—) 773 K (top) and detail of the 773 K curve showing the weight gain and loss at early times (bottom).

A weight gain systematically occurs in a first step. For materials exhibiting only an active oxidation behavior like carbon, such a weight increase can only be related to a sorption process that is activated when the oxidizing environment is introduced. TPD-MS analysis of oxidized samples (Figures 1b and 1c) shows that the oxidation process leads to the formation of a significant amount of surface groups. The profiles of CO and CO₂ desorption shows that ethers are present together with anhydrides and lactones [16]. The amounts of oxygenated functions are similar for samples oxidized in wet or dry air.

When sorption reaches saturation through a constant thickness of material, the overall weight variation tends to a linear decrease versus time, generally once -0.5 % of burn-off is reached. The oxidation rates were determined from a linear regression of the $\Delta m/S$ curves versus time, within a -0.5 to -2% range of burn-off. . In this domain of weight loss, the recession of the sample surface is uniform in function of time and it doesn't lead to a modification of the whole reactive surface area. The values of reaction rates recorded for each temperature have been reported on an Arrhenius plot (figure 6). A value of the apparent activation energy can thus be deduced (table 4). In dry air, the values of activation energy remain similar whatever the oxygen concentrations. The same trend is obtained in wet air.

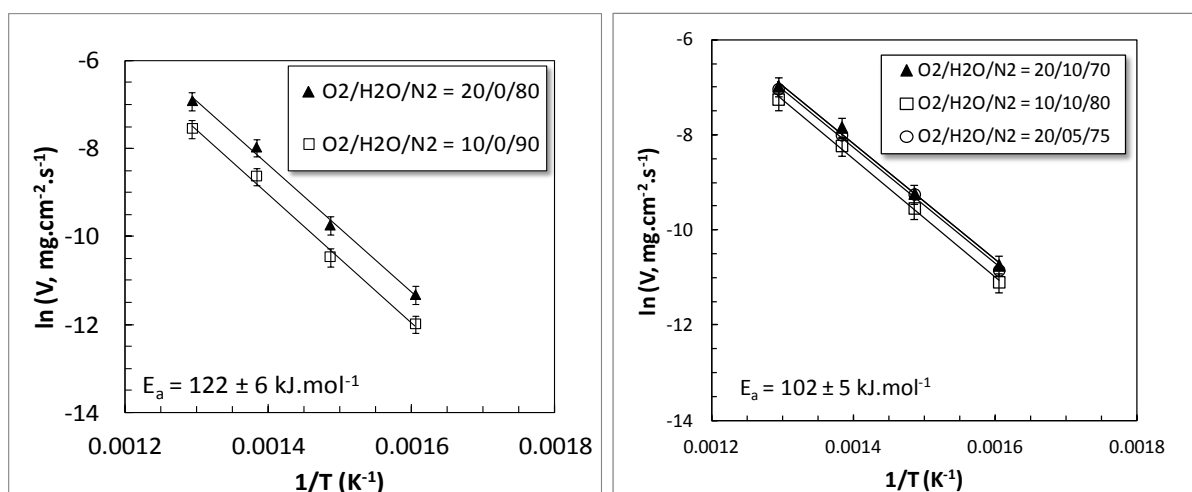


Figure 6: Arrhenius plots showing the oxidation rates of phenolic resin-based carbon samples under atmospheric pressure; in dry gas mixtures (left) and in wet environment (right).

The reaction rate is dependent on the reactive partial pressures of oxygen and moisture (equation (1)). To determine the reaction orders, experiments were performed at 673 K under different reactive environments, controlled in O₂ and H₂O partial pressures (figure 7). The Arrhenius plot apparently does not indicate any change in the oxidation mechanism in the considered temperature range.

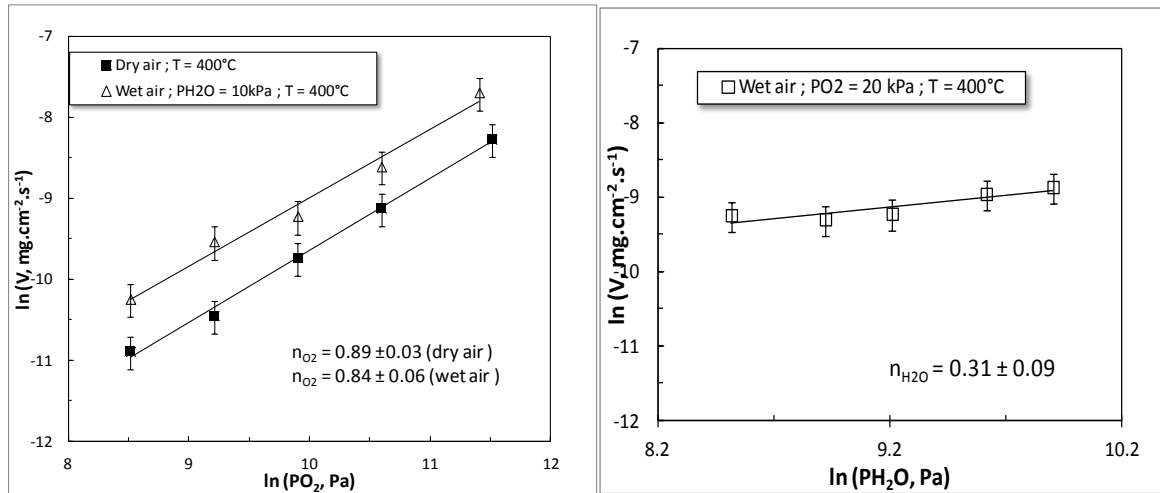


Figure 7: Plot of the C -carbonized oxidation rates versus the partial pressure of oxygen (left) and water vapor (right), at 673 K.

The parameters describing the kinetic law at 673 K are gathered in table 4. It is interesting to note that the activation energy of oxidation is lower in wet air than in dry air. The values of the partial reaction order related to oxygen remain very close for both dry and wet air.

Table 4: Kinetic law parameters of the oxidation rate of phenolic resin-based carbon obtained under dry and wet air at 673 K

Parameters	Dry Air	Wet Air
E_a (kJ/mol)	122 ± 6	102 ± 5
k_0 ($\text{mg} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-\sum_i n_i}$)	27.7	0.128
n_{O_2} : Partial order related to O_2	0.89 ± 0.03	0.84 ± 0.06
$n_{\text{H}_2\text{O}}$: Partial order related to H_2O	-	0.31 ± 0.09

To better understand the role of each reactive gaseous species on the recession process, the oxidation rates at 773 K in different oxidizing environments have been compared (table 5). In wet air, the contribution of moisture to the oxidation rate remains very limited in regard to the role of oxygen. The rate is indeed 10% higher for a 50% increase of the oxidation species concentration (Table 5). Such a result is indicative of a smaller value of the reaction order related to moisture compared to O_2 . The comparison of the reaction rates shows that the oxidation of C -carbonized in a mixture of water vapor and nitrogen at this temperature is negligible. Yet, in a pure H_2O environment, the oxidation/corrosion rate is neatly decreased. The difference in the oxidative capability of oxygen and water vapor is thus clearly shown.

Table5: Variation of oxidation rates of C-carbonized with oxidizing environment (773 K)

Composition of oxidizing environment O ₂ /H ₂ O/N ₂	Oxidation rate mg/cm ² .s
20/0/80	1.06 10 ⁻³
20/10/70	1.17 10 ⁻³
0/10/90	0.001 10 ⁻³

Surface characterizations

Figure 8 presents SEM of the C-carbonized surface before and after oxidation. The images illustrate the smoother surface of oxidized C-carbonized, as compared to the raw material and highlight the creation of large cracks. No significant difference was found in the cracking behavior of the samples in dry or wet air. A similar cracking phenomenon associated with a drop of the mechanical properties was reported for bulk “glassy carbon” obtained by resin carbonization at 1273 K [25]. The authors concluded that chemisorption of oxide species at 773 K in air leads to increase the coefficient of thermal expansion in surface that induces cracking on cooling.

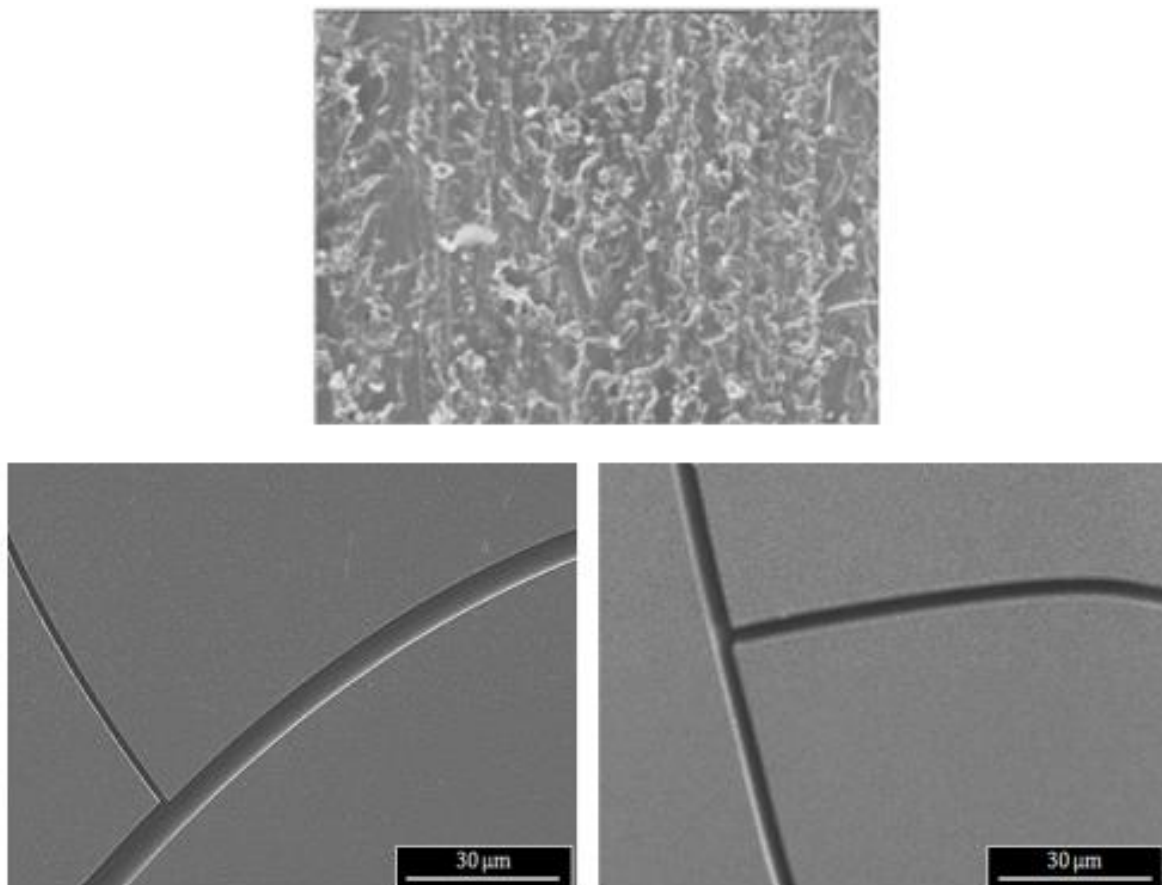


Figure 8: SEM micrographs of C-carbonized before (top) and after oxidation 3h at 773 K in dry air (bottom left) and wet air (bottom right).

The active surface areas (ASA) of C_{-carbonized} samples were measured as described in the experimental part before and after oxidation in dry or wet air. The carbon samples were all treated at 673 K during the proper time to reach 5% of the burn-off level. The values (table 6) are higher after oxidation but very close for the both oxidation conditions.

Table 6: Active surface area values of C_{-carbonized} and C_{-carbonized} oxidized at 673 K for 5% burn-off level

Sample	ASA (m ² /g)
C _{-carbonized}	1.56
C _{-carbonized} oxidation in dry air	5.74
C _{-carbonized} oxidation in wet air	5.71

3. Discussion

Characterization

The structural analyses show that the pyrolysis of phenolic resin in the conditions used in this work produces a carbonaceous material that can be classified as non-graphitizable carbon. It exhibits a disordered structure that is close to that of similar materials, as described in previous works [6,22,24,27].

It is interesting to notice that, besides, the oxygen concentration measured by XPS varies along the cross-section of the samples. A higher concentration was indeed measured close to the carbon surface of the samples, compared to the bulk (table 2). The presence of oxygen in depth, 2.1nm below the surface of furan resin-derived carbon heat treated at 1473 K, has been reported [27]. Furan resin is an oxygen-containing carbon precursor that also results, after pyrolysis, in a non-graphitizable carbon. Such a type of carbon is comparable to phenolic resin-based coke, as confirmed by Raman analyses. The presence of oxygen results from the incomplete carbonization of phenolic resin at 1273 K. The heterogeneous distribution of oxygen through the sample thickness can be explained by the different pyrolysis gas evolution rates.

The structural organization of C_{-carbonized}, as characterized by Raman spectroscopy (figure 4), is also distinct between the surface and the bulk. The parameters describing the carbon Raman features (table 3) show that carbon is less organized close to the surface. Such a disorder is correlated with the presence of defects that can be typically associated to chemical bonds with heteroatoms. The evolution of the structural properties across the specimen section can likely be correlated with the oxygen concentration gradient. The presence of a larger amount of oxygen functions close to the surface, as shown by XPS analysis, may be partly responsible for the lower structural organization state.

The value of ASA for C_{-carbonized} (1.56 m²/g) is higher than values typically reported for carbonaceous materials having a higher structural organization, such as pitch-derived carbons (around 0.2 m²/g)[9]. This result is consistent with the poorly organized structure of the external layer of the carbon material considered in this work, as with its the relatively high concentration of residual oxygen.

Oxidation in dry air

The general oxidation behavior of C_{-carbonized} in dry air at temperatures ranging from 623 K to 773 K, is comparable to that already reported for similar materials [27, 28]. The kinetic data determined in this work are representative of the complex reaction mechanisms involved during the oxidation of non-graphitizable carbon. The oxidation kinetic rates of resin-based carbon at temperature below 773 K are related to a particularly complex oxidation mechanism involving the formation of oxygen complexes, the interaction of oxidizing species with pre-oxidized surfaces and the defects of the carbon structure. The value of the activation energy (122 kJ/mol) is relatively low for carbon oxidation, and significantly lower than that previously reported for a phenolic resin-derived carbon oxidized in similar conditions (175 kJ/mol) [6].

The surface characteristics of these various samples play a key role in the oxidation mechanisms [27]. The surface characteristics of samples tested in reference [6] are not sufficiently detailed to properly compare the results and allow identifying the more reactive sites that are involved in the present case. Furthermore, the oxidation rates given in reference [6] were determined after less than 0.1 % burn-off while in this study they were obtained for burn-off ratios comprised between 0.5 and 2%, once a steady-state oxidation regime is established. This precaution was taken to ensure that the oxygen sorption phenomenon occurring at the beginning of the test had attained a saturation regime to balance the oxidation process [27,28].

The reaction order related to O₂ is in the same range as values previously published on other non-graphitizable carbons [8,11]. The data recorded can be discussed in regard to the oxidation mechanisms already reported for similar materials. For example, the mechanism proposed for the oxidation of furan resin-derived carbons at 773 K follows two main steps: (i) the distribution by surface diffusion and reaction of O₂ at the surface and under the surface of the sample and (ii) the recession of the surface, controlled by the thermally activated oxidation reaction, leading to the departure of CO₂ and a weight loss. The authors point out that the presence of oxygen functions pre-existing at the surface and under the surface of the sample, promotes the formation of new unstable oxygen complexes that can easily form CO₂ molecules [28]. A similar sorption process is also reported for other layered crystal structures such as hexagonal boron nitride form (h-BN), especially when the crystallization degree is low [29]. The sorption rate is limited by diffusion through the porosity and decreases regularly versus time. The linear weight loss is observed only when both sorption and oxidation rates become equal, the weight loss corresponding to the overall oxidation reaction [29]. A similar phenomenon is likely to occur during the oxidation of phenolic resin-based carbon at temperature below 773 K. Surface oxygen complexes are first formed by chemisorption on active sites, followed by carbon gasification. The data shown in table 6 and figure 5 are consistent with this hypothesis. The smooth surface of C_{-carbonized} observed after 3h of oxidation at 773 K (figure 8) is a consequence of carbon gasification. The cracks observed could result from the relaxation of internal stresses generated during pyrolysis. This effect is probably due to a differential shrinkage in the bulk and near the surface, possibly influenced by the elimination of the pyrolysis gases from the solid and related to the distinct physico-chemical properties of the bulk and the near surface material. The heterogeneity

between the surface and the bulk in both oxygen composition and structural state of $C_{\text{-carbonized}}$ could be the cause of internal stresses related to the oxidation process. A similar cracking process has been reported in hexagonal-BN coating having a low degree of crystallization [29].

To better investigate the relation between the oxidation mechanism and the degree of crystallization, some specimens of $C_{\text{-carbonized}}$ have been heat-treated up to 1873 K before being oxidized in dry air. The resulting $C_{\text{-1873}}$ samples are characterized by an O/C atomic ratio of 0.11, as measured from the outer surface and 0.005, 14 nm under the surface. The value of the ASA is $0.05 \text{ m}^2/\text{g}$ and the Raman measurements from parts of the specimen located close to the surface and in the bulk lead to $\text{FWHM}_D=95$ and 54 cm^{-1} , respectively. The results show that $C_{\text{-1873}}$ has a better organized structure than $C_{\text{-carbonized}}$, both close to the surface and inside the sample. The structural state of $C_{\text{-1873}}$ is also more homogeneous across the sample section than in the case of $C_{\text{-carbonized}}$. After heat treatment, the ASA is reduced by a factor around 30. The value of the oxidation rate measured during oxidation at 773 K under dry air, for a burn-off ranging from -0.5 to -2%, is $5.24 \cdot 10^{-5} \text{ mg/cm}^2\cdot\text{s}$. This value is significantly reduced compared to that measured before heat treatment. Such a trend has previously been observed by other authors in the carbon-derived materials from phenolic resin [6,28]. The morphology of the oxidized surface of $C_{\text{-1873}}$ is shown in figure 9. No crack formation is visible after oxidation. After a heat treatment up to 1873 K, the improvement of the crystalline structure seems to reduce considerably the oxygen sorption [29]. Furthermore, the more homogeneous structure and the changes of the physico-chemical surface features both contribute to decrease the oxidation rate and thus limit the degradation of the material.

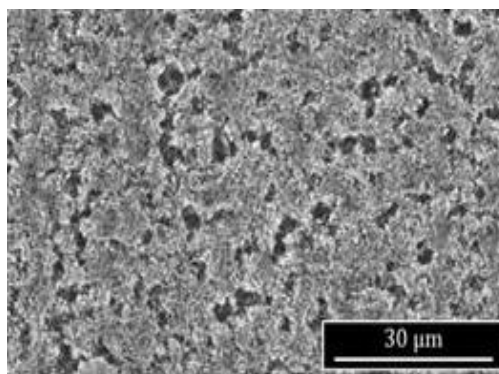


Figure 9 : SEM micrographs of $C_{\text{-1873}}$ after oxidation

Oxidation in wet air

The oxidation process of $C_{\text{-carbonized}}$ is apparently different in dry or wet air. The oxidation rate is slightly higher in wet air and the value of the activation energy is lower. On the other hand, the reaction order with respect to the H_2O partial pressure is lower in wet air than the reaction order related to O_2 (0.31 versus 0.84). Furthermore, the weight loss becomes negligible when $C_{\text{-carbonized}}$ is submitted to pure water vapor, nitrogen being added to keep constant the overall gaseous flow rate. This work has established that at moderate temperatures, typically less than 773 K, the presence of water vapor clearly influences the oxygen reaction process. Another work previously published [11] reports the same trends for the oxidation behavior of carbon fibers in both dry and wet environments in the same range of temperature.

The mechanism still remains difficult to describe in details. It is generally proposed that in wet air and below 1273 K, the adsorption of water vapor on the active sites of the carbon surface prevents the reaction with O₂; H₂O would therefore act as an inhibitor [8,9]. Below 773 K, interactions between water vapor and reactive sites would lead to hydroxyl groups. At low or moderate temperature, water can only achieve a dissociative chemisorption on the most reactive sites, hydroxyl functions can then be decomposed to semi-quinones which are very stables [30,31]. O₂ can adsorb on carbon at low temperature, as it is used for ASA measurements, leading to oxygenated functions with a wide range of thermal stability. Works from references [10] and [32] concluded that water vapor can react with oxygenated groups to form new functions that are more reactive with O₂ than the pristine oxygenated functions. It must be noticed that even at very low concentrations, impurities may have an influence on oxidation rate [6]. The presence of traces of sodium could enhance somewhat oxidation rate but the observation of carbon surfaces after oxidation under dry or wet air appears similar (figure 8) that suggesting that influence of impurities is not significant .

In regard to these works, an interpretation of our results can be proposed: in pure water vapor, if oxygenated and/or hydroxyl groups are formed by the reaction of H₂O with the initial reactive sites they are thermally stable, at least below 773 K. When H₂O is added to the O₂ gaseous environment, the resulting oxygenated groups are not as stable as the pristine O₂-derived functions. As a consequence, the role of the water vapor depends on the nature of oxygenated groups that are formed during the first step of the oxidation process. The initial proportion of carbon active sites is itself closely related to the structure of carbonaceous material (i.e. to the pre-annealing temperature) as well as the oxidation temperature. Hence, even if a comprehensive mechanism could not be proposed, this work concludes that intermediate species formed in different oxidizing conditions play a key role in the oxidation of phenolic resin-derived carbon at moderate temperatures.

4. Conclusions

The physico-chemical, structure and oxidation resistance of phenolic resin-based carbon heat treated up to 1273 K have been investigated. This carbon material can be classified in the non-graphitizable carbon category with a very poor degree of structural organization and significant heterogeneities in both structure and elemental composition through the samples cross-section. Oxidation experiments were performed at a temperature ranging from 623 to 773 K under dry and wet air. The oxidation rates and their activation energies and reaction orders related to O₂ and H₂O were determined from the TGA curves. The oxidation rate of the carbon material is considerably lower in pure H₂O than in pure O₂. However, when H₂O is added to O₂, the oxidation rate slightly increases and the value of activation energy becomes lower. These results suggest that, in wet air, water vapor would react with O₂-derived groups that are already present, to form more reactive functions.

This work has provided a better understanding of the oxidation behavior of a key constituent of a low-cost C/C composite in a seldom experimented temperature range. The temperature limit for a long-term use of this type of composites can also be better comprehended. The phenolic resin-based coke tested in this study is significantly more reactive than commercial

vitreous carbon. This behavior is related to the low pyrolysis temperature of the carbon specimens compared to the final heat treatment temperature usually applied to glassy carbons aimed at corrosive environments. The influence of the annealing conditions on the oxidation behavior of phenolic resin-based carbon could be explored in more details as a next step of this work.

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References:

- [1] N.R. Laine, F.J. Vastola, P.L. Walker Jr, The Importance of active surface area in the carbon-oxygen reaction, *J. Phys. Chem.*, 67 (1963) 2030-2034.
- [2] I.W. Smith, The intrinsic reactivity of carbons to oxygen, *Fuel* 57 (1978) 409-414.
- [3] P. Ehrburger, F. Louys, J. Lahaye, The concept of active sites applied to the study of carbon reactivity, *Carbon* 27 (1989) 389-393.
- [4] P.L. Walker Jr., R.L. Taylor, J.M. Ranish, An update on the carbon-oxygen reaction, *Carbon* 29 (1991) 411-421.
- [5] F.Rodríguez-Reinoso, P.L. Walker Jr, Reaction of glassy carbon with oxygen, *Carbon* 13 (1975) 7-10.
- [6] H.W. Chang, S.K. Rhee, Oxidation of carbon derived from phenolic resin, *Carbon* 16 (1978) 17-20.
- [7] A. Arenillas, F. Rubiera, C. Pevida, C.O. Ania, J.J. Pis, Relationship between structure and reactivity of carbonaceous materials, *J. Therm. Anal. Calorim.*, 76 (2004) 593-602.
- [8] P. Delhaes, Chapter 12: Chemical reactivity and surface treatment, in: *Carbon based solids and materials*, Hoboken, ISTE-Wiley ed., 2011, pp 462-480
- [9] C. Vix-Guterl, G. Bekri, J. Dentzer, S. Manocha, L.M. Manocha, P. Ehrburger, Reactivity in wet air of carbon-carbon composites with treated pitches, *J. Anal. Appl. Pyrolysis*, 67 (2003) 341-357.
- [10] J.C. Petit, Y. Bahadi, New insight on the chemical role of water vapor in the ageing of activated carbon. *Carbon* 31 (1993) 821-825.
- [11] X. Bertran, C. Labrugère, M.A. Dourges, F. Rebillat, Oxidation behavior of PAN-based carbon fibers and the effect on mechanical properties, *Oxid. Met.* 80 (2013) 299-309.
- [12] S.R. Dhakate, P. Bahl, P.D. Sahare, Oxidation behavior of PAN based carbon fiber reinforced phenolic resin matrix composites, *J. of Mater. Sci. Lett.* 19 (2000) 1959–1961.
- [13] A. Braun, M. Bärtsch, B. Schnyder, R. Kötz, O. Haas, H.-G. Haubold, G. Goerigk, X-Ray scattering and adsorption studies of thermally oxidized glassy carbon, *J. Non-Cryst. Solids* 260 (1999) 1–14.
- [14] N. Zouaoui, M. Labaki, M. Jeguirim, Diesel soot oxidation by nitrogen dioxide, oxygen and water under engine exhaust conditions: Kinetics data related to the reaction mechanism, *C. R. Chim.* 17 (2014) 672–680

- [15] A. Fredrik Ahlström, C.U. Ingemar Odenbrand, Combustion characteristics of soot deposits from diesel engines, *Carbon* 27 (1989) 475–483,
- [16] P. Brender, R. Gadiou, J.-C. Rietsch, P. Fioux, J. Dentzer, A. Ponche, C. Vix-Guterl, Characterization of Carbon Surface Chemistry by Combined Temperature Programmed Desorption with in Situ X-ray Photoelectron Spectrometry and Temperature Programmed Desorption with Mass Spectrometry Analysis, *Anal. Chem.* 84 (2012) 2147–53.
- [17] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, Modification of the surface chemistry of activated carbons, *Carbon* 37 (1999) 1379–89)
- [18] N. Iwashita, C.R. Park, H. Fujimoto, M. Shiraishi, M. Inagaki, Specification for a standard procedure of X-ray diffraction measurements on carbon materials, *Carbon* 42 (2004) 701-714.
- [19] B.E. Warren, X-Ray diffraction in random layer lattices, *Phys. Rev.*, 59 (1941) 693-698.
- [20] J.-M. Vallerot, X. Bourrat, A. Mouchon, G. Chollon, Quantitative structural and textural assessment of laminar pyrocarbons through Raman spectroscopy, electron diffraction and few other techniques *Carbon*, 44 (2006) 1833-1844.
- [21] P. Weisbecker, A. Guette, Thin film preparation of C/C composites and CMC using the broad Argon Ion beam method. In: Proceeding of ICCM-17 Conference, Edinburgh (United Kingdom) 2009.
- [22] M. Zancanaro, N. Bertrand, F. Rebillat, Definition of optimized conditions to extract accurate kinetic laws from tga experiments: modeling and validation, in: D. Pint, D. Monceau, M. Vilasi, S. Chevallier, Y. Wouters and C. Desgranges (Eds.), Proceedings of HTCPM 9th International Symposium, , CEFRACOR-EFC, 2016, pp. 144-145.
- [23] Z.L. Zhang, R. Brydson, Z. Aslam, S. Reddy, A. Brown, A. Westwood, B. Rand, Investigating the structure of non-graphitising carbons using electron energy loss spectroscopy in the transmission electron microscope, *Carbon* 49 (2011) 5049-5063.
- [24] T.H. Ko, W.S. Kuo, Microstructural changes of phenolic resin during pyrolysis. *J. Appl. Polym. Sci.* 81 (2001) 1084-1089.
- [25] W.D. Liu, M. Liu, L.C. Zhang, Oxidation-induced mechanical deterioration and hierarchical cracks in glassy carbon, *Carbon* 100 (2016) 178-186.
- [26] S.S. Tzeng, Y.G. Chr, Evolution of microstructure and properties of phenolic resin-based carbon/carbon composites during pyrolysis. *Mater. Chem. Phys.*, 73 (2002) 162-169.
- [27] M. C. Ma, B. S. Haynes. Surface heterogeneity in the formation and decomposition of carbon surface oxides, in: proceeding of the twenty-Sixth Symposium (International) on Combustion/The Combustion Institute, 1996, pp. 3119–3125.
- [28] K.Nakamura, Y. Tanabe, M. Fukushima, Y. Teranishi, T. Akatsu, E. Yasuda, Analysis of surface oxidation behavior at 500 °C under dry air of glass-like carbon heat-treated from 1200 to 3000 °C. *Mater. Sci. Eng. B*, 161 (2009) 40-45.
- [29] S. Willemin, P. Carminati, S. Jacques, J. Roger, F. Rebillat, Identification of complex oxidation/corrosion behaviors of boron nitride under high temperature. Submitted to *Oxidation of Metals*.
- [30] J.-C. Rietsch, P. Brender, J. Dentzer, R. Gadiou, L. Vidal, C. Vix-Guterl, Evidence of water chemisorption during graphite friction under moist conditions, *Carbon* 55 (2013) 90–97.

- [31] M. Oubal, S. Picaud, M.-T. Rayez, J.-C. Rayez, Interaction of water molecules with defective carbonaceous clusters: An ab initio study, *Surf. Sci.* 604 (2010) 1666–1673.
- [32] Q.L. Zhuang, T. Kyotani, A. Tomita, The change of TPD pattern of O₂-gasified carbon upon air exposure. *Carbon* 32 (1994) 539-540.